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# A STUDY OF CHEMICAL INTERFERENCES IN THE ANALYSIS OF N-NITROSODIMETHYLAMINE IN ENVIRONMENTAL SAMPLES.

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N-nitrosodimethylamine (NDMA) is also known as dimethylnitrosamine (DMNA) and N-methyl-N-nitrosomethanamine. NDMA can be present as a trace contaminant in industrial processes and in products manufactured using dimethylamine. It may also be found in various foods such as cured or smoked meats, beverages such as beer and in tobacco smoke condensates. In addition, NDMA has been found in some ion exchange resins. NDMA has been found to be carcinogenic in the mouse, rat, hamster, guinea-pig, rabbit and rainbow trout and is a suspected human carcinogen. Because of the suspected toxicity and carcinogenicity of NDMA, the interim drinking water guideline has been set by the Ontario Ministry of the Environment (MOE) at 9 ppt.

NDMA can be analyzed by a number of methods including gas chromatography (GC) followed by thermal energy analysis (TEA), low resolution mass spectrometry (LRMS) or high resolution mass spectrometry (HRMS).

The sensitivity of the instrumentation is sufficient to meet the drinking water guideline. However, the degree of selectivity required of the detection system may be predicated by the degree of sample cleanup utilized.

The sample preparation protocol developed at MOE was designed to be simple. Since NDMA is a neutral compound, the sample cleanup, after extraction from the matrix, is a partitioning scheme that removes the basic and acidic components from the extract. A summary of the protocol is outlined below:

$d_6$-NDMA is added to the sample as the internal standard. Filtration is used to remove any particulates that may be present. After the pH is adjusted to 12 to keep the acidic components in the aqueous phase, the basic solution is serially extracted with dichloromethane. The dichloromethane extract is washed with a sulphuric acid solution to remove basic components from the organic phase. The washed extract is filtered through granular anhydrous sodium sulphate to remove water and is then concentrated by rotary evaporator and a nitrogen evaporating unit.

The sample extract contains the remaining neutral organics and no further cleanup is done to separate neutrals from neutrals.

The sample extracts were analyzed by GC/LRMS and GC/HRMS.

The mass spectrum of NDMA consists of 2 major ions, the molecular ion at m/z 74 and an intense fragment ion at m/z 42. Selected ion monitoring (SIM) analysis of NDMA by GC/LRMS was limited to a quantitation ion at m/z 74 and a single qualifying ion at m/z 42. The acceptable ratio of m/z 42:74 was set at +/- 20% of the ratio obtained from a calibration standard run on the same instrument.



The mass resolution requirements for HRMS were determined as follows:

The exact masses for NDMA and a common ester fragment are m/z 74.0480 ($C_2H_6N_2O$) and m/z 74.0368 ($C_3H_6O_2$), respectively. The mass resolution required to differentiate these masses is 6,607 [74/(74.0480-74.0368)]. Operation of a high resolution mass spectrometer at 7,000 resolving power (RP) allows NDMA to be differentiated from chemical interferences such as $C_3H_6O_2$.

On a single quadrupole mass spectrometer, which is restricted to low resolution mass spectrometry (LRMS), ions having the empirical formulae $C_2H_6N_2O$ and $C_3H_6O_2$ are indistinguishable from each other because they both have m/z = 74. Therefore qualifying ion(s) must be used and the ratio of the qualifying ion to the quantitation ion must be within acceptable limits.

On a high resolution mass spectrometer, single ion monitoring of the accurate mass m/z 74.0480 provides sufficient selectivity to distinguish NDMA from chemical interferences.

Instrumental conditions were as follows:

| | **GC/LRMS** | **GC/HRMS** |
|---|---|---|
| GC | HP5890 | Varian 6000 |
| MS | VG Trio-2 or HP 5970 MSD | VG ZAB-2F |
| Column | DB-1701 (30 m) | DB-1701 (30 m) |
| Electron energy | 70 eV | 70 eV |
| Ions monitored | m/z 42, 74 (NDMA)<br>m/z 46, 80 ($d_6$-NDMA) | m/z 74.0480 (NDMA)<br>m/z 80.0857 ($d_6$-NDMA)<br>m/z 68.9952 (PFTBA)(lockmass) |

Analyses of drinking water samples were undertaken. A comparison of analyses of drinking water extracts is shown in the following table:

**LRMS vs HRMS Data (ug/L)**

| **Sample** | **LRMS-A** | **LRMS-M** | **HRMS** |
|---|---|---|---|
| 1. | 0.025 | 0.016 | 0.019 |
| 2. | 0.023 | 0.015 | 0.012 |
| 3. | 0.017 | 0.011 | 0.011 |
| 4. | ----- | 0.011 | 0.013 |
| 5. | ----- | 0.034 | 0.019 |

A = automatic areas
M = manual areas

These data demonstrate that:

(1) automatic areas are dependent on the peak/baseline detection parameters chosen and the peak widths of overlapping interferences; peak areas may have to be determined manually (compare samples 1-3).

(2) neutral chemical interferences in drinking water samples co-elute with NDMA.

(3) confirmation by HRMS may be required.

Further studies included other matrices as shown in the following table:

**LRMS vs HRMS Data (ug/L)**

| Sample | LRMS | HRMS |
|---|---|---|
| 1. Spiked HPLC-grade water | 0.49* | 0.42 |
| 2. STP influent | 0.43 | 0.40 |
| 3. STP influent | 0.11* | 0.02 |
| 4. STP influent | 0.20* | 0.24 |
| 5. Groundwater | ND | 0.09 |
| 6. Groundwater | 1600* | 170 |
| 7. Industrial effluent | 0.37* | 0.26 |

* interference (incorrect ratio of m/z 42:74)
ND = not detected (no peak)

These data demonstrate that:

(1) neutral chemical interferences in other matrices co-elute with NMDA.

(2) confirmation or analysis by HRMS may be required.

Full scan GC/LRMS of a groundwater (sample 6) was undertaken to identify some of the neutral chemical interferences.

Chlorobenzene, ethylbenzene and xylenes were found to be present. Chlorobenzene and ethylbenzene co-elute with NDMA and $d_6$-NDMA. The xylenes elute after NDMA but can co-elute if present in sufficient concentrations.

These compounds have minor ions at m/z 74 and will interfere with the m/z 74 of NDMA. The mass resolution required to differentiate them from NDMA is 2,285. Operation of the HRMS at 7,000 RP is sufficient for this differentiation.



With the present level of sample cleanup, the ratio of m/z 42:74 that is used as a criterion for positive identification of NDMA by LRMS is of limited utility because it is frequently outside of the +/- 20% window even in relatively clean samples such as drinking water or laboratory procedure blanks. In some cases, this is due to interferences at m/z 42. However, interferences can also be detected at m/z 74 or m/z 80. In these cases, the quantitation will be adversely affected. For LRMS to be a viable technique, a more rigorous sample cleanup (separation of neutrals from neutrals) and possibly better chromatography are necessary.

Single ion monitoring by LRMS does not afford sufficient selectivity for a positive identification of NDMA. Therefore, a protocol that utilizes a minimum number of sample preparation steps requires confirmation, or analysis by HRMS for positive identification and accurate quantitation.